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A LABORATORY STUDY OF THE TREATMENT OF ALPHA TNT WASTES WITH IRON FILINGS

By

F. W. Norris, Assistant Sanitarian (R),
C. C. Ruchhoft, Principal Chemist and
S. Megregian, P. A. Sanitarian (R)

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Experiments by Mr. D. A. Reedy, of the Bluebonnet Ordnance Plant at McGregor, Texas, indicating that iron filings would remove alpha TNT from waste water, led to this study. Other methods of alpha TNT removal from waste water (1) (2) have not been economically adaptable to all conditions, therefore, an attempt was made to determine the optimum conditions for removal of alpha TNT from the waste of shell and bomb loading plants by the above method.

In a series of preliminary experiments, alpha TNT in water was passed over a parallel arrangement of two filter tubes (one inch in diameter and filled with twelve inches of iron filings). One filter was "activated" by allowing it to remain in contact with a 1% solution of HCl for one hour, the other filter was filled with distilled water for the same length of time, after which both were washed with fresh distilled water. A solution containing 115 p.p.m. of alpha TNT was allowed to percolate through both filters at an average rate of 0.5 ml. per minute, maximum rate, 3.3 ml. per minute. Both filters became clogged after 15 liters of solution had passed through. The filtrate contained no alpha TNT. An analysis of the first two liters of filtrate from each filter is presented in Table I.

Table I

Analysis of filtrate from Filters A and B

	pH	Total Solids p.p.m.	Ash p.p.m.	Kjeldahl N p.p.m.	B.O.D. p.p.m.	Ammonia N p.p.m.	O.C.(1) p.p.m.	Iron p.p.m.
Alpha TNT Solution	7.4	212	72	2.6	0.0	0.6	0.0	0.7
Filtrate - Filter A	9.0	278	96	12.8	4.6	2.4	62.0	16.3
Filtrate - Filter B	9.7	208	84	12.0	2.8*	1.2	56.0	0.2+

* Average of four dilutions.
Filter A - Iron filings pretreated with 1% HCl.
Filter B - Iron filings pretreated with distilled water only.
(1) - Oxygen Consumed

These results show a significant increase in both Kjeldahl nitrogen, ammonia nitrogen, pH, oxygen consumed, and B.O.D. The increase in recovered nitrogen and B.O.D. indicate that possibly some of the NO_2 groups in alpha TNT had been reduced. This was also evident by the increase in pH. The treatment of Filter A with HCl had very little effect on the character of the filter effluent.

As the filtrate came through the filters its color was low but increased on standing. The increase in color, as measured by the visual spectrophotometer at several wave lengths, was rapid during the first seven hours and then continued at a lower rate for several days when readings were discontinued. A slight turbidity developed after 48 hours and a brown precipitate was observed after 27 days. The color of the supernatant after 27 days had decreased to the value observed at the 2 hour interval while the pH during the 27 days dropped from 9.0 to 6.6.

Several standard water treatment methods, such as coagulation, aeration, ozonation, chlorination and activated carbon, were applied to the fresh filtrate to remove the color. Of these methods, ozonation produced a marked reduction in color after 15 minutes of treatment. Chlorination had a variable effect, a small dose, 1.5 p.p.m., produced a reduction in color. Increased doses up to 75 p.p.m. increased the color. When 150 p.p.m. was added a precipitate formed which produced a colorless supernatant after it had settled out. The other methods were unsatisfactory.

Solubility experiments on the residue of the filtrate after evaporation produced the following results: Insoluble in ether, chloroform, benzene, xylene, acetone, butyl and amyl alcohols. Slightly soluble in water,

methyl and ethyl alcohols. Soluble in acids; insoluble in alkalis.

Upon treating the residue with water and centrifuging, a brown residue resulted which was insoluble in all the above solvents except sulphuric and nitric acids. On determining a melting point, the material decomposed near 300° C.

In a quantitative experiment to determine the amount of alpha TNT removed by iron filings, two filters were set up containing 553 gms. and 243 gms. respectively of iron filings. These filters were run intermittently for 65 days at an average rate of 1071 and 768 ml. per day. Complete TNT removal was effected during this period and the first sign of incomplete removal was observed on the final day, when effluents from both filters gave a positive test for alpha TNT. A summary of the data collected during the filter run is listed in Table II.

Data in Table II show that a total of 6,545 mg. of alpha TNT was removed from 69,590 ml. of TNT water by Filter A, and 4,361 mg. from 49,930 ml. by Filter B. This shows a total removal of .18 mg. of TNT per gram of iron per day for Filter A and .28 mg. of TNT per gram of iron per day for Filter B, or an average total removal of .29 pounds of TNT per ton of iron per day. Preliminary results showed that for short periods, the filters would remove TNT at about nine times the average rate shown above.

Using a hypothetical case in which a daily discharge of 50,000 gallons of waste containing 50 p.p.m. of alpha TNT is treated by the above method, the following calculations are of interest:

50,000 gal. of waste containing 50 p.p.m. TNT will discharge 20.84 pounds per day. Using average figures from the data above, 398 gms. of iron filtered .92 liters per day therefore: $\frac{50{,}000 \times 3.785 \times 398}{.92 \times 454 \times 2000}$ = 90.2 tons of

iron would be required to filter 50,000 gallons of waste daily.

Table II
Removal of Alpha TNT from Solution by Iron Filings

Alpha TNT Dosed p.p.m.	No. of Days Run	Ave. Ml. Dose Per Day		Total Volume - Ml.	
		A (1)	B (2)	A (1)	B (2)
78.8	17	533.5	465.2	9,070	7,910
64.0	9	888.8	944.4	8,000	8,500
64.0	2	1,260.0	1,010.0	2,520	2,020
82.9	3	750.0	1,550.0	6,000	12,400
73.6	6	1,900.0	833.3	11,400	5,000
142.3	4	1,575.0	1,125.0	6,300	4,500
129.3	9	1,666.7	500.0	15,000	4,500
87.5	10	1,130.0	510.0	11,300	5,100
Total Volume				69,590	49,930
Total Mg. Alpha TNT Filtered				6,545	4,361
Mg. Alpha TNT removed per g. Iron				11.8	17.9
Mg. Alpha TNT removed per g. Iron per day				.18	.28
Av. Rate of Flow, ml. per day		1,071.0	768.0		

(1) Filter A contained 553.5 g. of iron filings.

(2) Filter B contained 243.2 g. of iron filings.

From the above data, 1 gm. of iron will remove a total of .0149 gm. of TNT. Thus, 90.2 tons will remove 2687 pounds of TNT during its lifetime as a filter. At a daily rate of 20.84 pounds, a filter of 90 tons will last 129 days.

Using the packing area in Filter B which contained 243.2 gms. of iron, the filter vol. occupied by the iron was $(1/2)^2 \times \pi \times 12$ cu. in. or 9,4248 cubic inches. The area occupied by 90 tons of iron would then be:

$$90.2 \text{ Tons} = \frac{81,878,500 \text{ g} \times 9.4248}{243.2} = 3,173,061 \text{ cu. in.}$$
$$= 1,836.3 \text{ cu. ft.}$$
$$= 68 \text{ cu. yds.}$$

The iron filings on Filter B were washed in water and acetone, dried, and weighed. An increase in weight was observed and this was believed due to incomplete removal of the collected material on the filings by water and acetone treatment. An analysis of the washings gave the following results:

	Total Solids	% Volatile	% Ash	% Iron	% Insoluble in HCl
Water	12.1654 g	16.5	83.5		
Acetone	1.2265 g	20.7	79.3	53.1	.7

The filings from Filter A were divided into an upper and lower fraction and the separate portions were washed in water and acetone and the washings evaporated. The residue was analyzed as shown in Table III. The TNT solution was removed from the filter before washing, and evaporated.

Table III
Analysis of washings from Filter A

	Weight g.	% Ash	% Volatile	% Iron	% (3) C	% (4) N	% Volatile as C	% Volatile as N
Upper	3.9473	85.2	14.8	81.5	8.7	1.7	55.4	8.4
Lower	7.9584	84.5	15.5	77.1	8.6	1.0	58.1	4.7
TNT Solution	.8468	70.0	30.0	69.3	11.8	4.0	38.3	10.2

(3), (4) see References.

The residue obtained from the evaporation of the effluent from Filter A was found to decompose without melting at 250-300° C. An elementary analysis of the residue gave the following:

Element	Percent	Proportion
C	50.4+	7.4
H	3.1	5.4
N	8.0	1.0
O *	38.5+	4.2

* by difference

\+ average of wet and dry combustion methods.

In order to determine whether 2, 4, 6 Tri-amino-toluene was one of the end products of the reduction, iron was added to this compound and the mixture aerated. Spectrophotometric examinations showed a close correlation with the TNT effluent, thus leading to the conclusion that 2, 4, 6 Tri-amino-toluene may be present in the effluent after filtration through iron.

Summary

Experiments were performed to determine the practicability of removing alpha TNT from water with iron filings. In preliminary experiments, it was observed that alpha TNT was completely removed from solution by a one inch diameter filter with a twelve inch depth of iron filings. Quantitative experiments indicated that an average dose of 920 ml. per day of waste can be treated by 398 g. of iron filings for 65 days before the filtrate shows the presence of TNT, and a total of 5.453 g. of TNT can be removed before it becomes necessary to replace the iron. Short time filtrations will remove about nine times the average daily rate indicated.

The filtrate obtained from the treatment showed an increase in ammonia and Kjeldahl nitrogen, B.O.D., and pH. A gradual color develop-

ment was observed which on long standing became turbid and precipitated out. Ozonation or heavy chlorination aided in removing filtrate color.

Spectrophotometric examinations suggested that some of the alpha TNT passing through the filter may be converted to the tri-amino compound.

Conclusions

From the above data it is apparent that in order to treat this waste by iron filtration, a small filter of about 600 sq. ft. in area and about 3 ft. deep must be built and refilled about three times a year with scrap iron shavings. Assuming the cost of scrap iron shavings, including transportation and handling to be about $20 a ton, the annual cost for iron would be about $5400. Adding the cost of disposal of the waste iron and other handling costs, the expense of this method of treatment is quite high when compared to the cost of activated carbon treatment. This cost was pointed out in (1) as between $4.50 and $15.00 per day for a 50,000 gallon daily waste. Carbon treatment would then cost between $1,600 and $5,400, and the methods of handling carbon sludge are much simpler and less expensive than that required to replace 90 tons of iron shavings three times a year.

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